



NRL/MR/6180--06-8960

Examination of JP-8 Fuels for Contaminants Responsible for KC-130J Nozzle Fouling

ROBERT E. MORRIS

KEVIN J. JOHNSON

*Navy Technology Center for Safety and Survivability
Chemistry Division*

CHRISTINA DIGIULIO

*Nova Research, Inc.
Alexandria, VA*

May 16, 2006

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 16-05-2006		2. REPORT TYPE Memorandum Report		3. DATES COVERED (From - To) February 6 - March 3, 2006	
4. TITLE AND SUBTITLE Examination of JP-8 Fuels for Contaminants Responsible for KC-130J Nozzle Fouling				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Robert E. Morris, Kevin J. Johnson, and Christina DiGiulio*				5d. PROJECT NUMBER	
				5e. TASK NUMBER 61-M898-0-6-5	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory, Code 6181 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6180--06-8960	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Air Systems Command Fuels and Lubricants Division, Air 4.4.5 22229 Elmer Road, Unit 4 Patuxent River, MD 20670-1534				10. SPONSOR / MONITOR'S ACRONYM(S) NAVAIR	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES * Nova Research, Inc., 1900 Elkin Street, Suite 230, Alexandria, VA 22308					
14. ABSTRACT This examination was conducted at NRL to determine if fuel contamination was responsible for premature fuel nozzle coking on USMC KC-130J and USAF C-130J aircraft deployed in Iraq. The overall chemical compositions of the 26 JP-8 samples were found by chemometric modeling to be within the range of compositions determined in the 240 worldwide JP-8, JP-5, and Jet A fuels currently in our reference fuels database. This result was obtained from analyses by both gas chromatography and NIR spectroscopy. The analysis did reveal normal batch to batch variations between the fuels sampled from the storage facility at Aqaba and those sampled further down the supply chain at the Al Asad airbase. Further analyses by GC, NIR, and GC-MS did not detect the presence of detectable levels of any contaminants or otherwise abnormal fuel components, including the dust abatement polymer used at this airbase.					
15. SUBJECT TERMS Mobility fuel Nozzle fouling Fuel Chemometrics GC NIR Jet fuel Nozzle coking JP-8 Modeling GC-MS PLS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 16	19a. NAME OF RESPONSIBLE PERSON Robert E. Morris
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (202) 767-3845

CONTENTS

1.0 OBJECTIVE	1
2.0 BACKGROUND	1
3.0 EXPERIMENTAL	1
4.0 RESULTS AND DISCUSSION	4
5.0 SUMMARY	12
6.0 CONCLUSIONS.....	12
7.0 ACKNOWLEDGEMENT	12

FIGURES AND TABLES

Figure

1	PCA of NIR fuel data. A scores plot of PC1 vs PC2 shows similarity of USMC JP-8 fuels to specification reference fuels and a JP-8 fuel from the Patuxent River NAS (PAX).	5
2	Scores plot from PCA of USMC fuels (in red), compared to reference fuels (green) and the PAX JP-8.	6
3	Scores plot of PC4 vs PC1 from PCA of the USMC fuels (in red), compared to reference fuels (green) and the PAX JP-8, showing similarities to reference fuels and discrimination of two batches within the USMC JP-8 fuel set	6
4	Detail from Figure 3, showing a clear distinction between the fuels sampled from the supply depot on December 25 and the fuels sampled at Al Asad on December 30, while still within the normal fuel composition range of the reference fuels	7
5	Scores plot from PCA of GC data, showing distinction between fuels sampled on two different dates, similar to that previously seen in scores plots of NIR data	7
6	Scores plot from PCA of ICP-atomic absorption elemental analysis data, showing similar distinctions between the two different fuel batches	9
7	Oxygen consumption of the USMC JP-8 fuels, showing similar thermal autooxidation stability characteristics compared to specification JP-5 fuels. A thermally unstable fleet sample contaminated with copper and an aged fuel sample are also shown for comparison.....	10
8	Detection of Envirotac II® by GC-MS through selected ion monitoring of the characteristic fragment at $m/Z=221$, compared to neat methylene chloride (Fig. 8A) and to fuel sample #5 (Fig. 8B).	11

Table

1	Set of 26 fuels sampled from the Al Asad fuel supply chain	2
2	ICP-AA elemental analyses of the fuel sample set, showing those elements detected used in the PCA. Elements analyzed for and found to be below the lower detection limits were not used for PCA. Results are given in $\mu\text{g/kg}$	8

EXAMINATION OF JP-8 FUELS FOR CONTAMINANTS RESPONSIBLE FOR KC-130J NOZZLE FOULING

1.0 OBJECTIVE

The objective of this study was to examine a sample set of 26 jet fuels to determine if compositional aspects of these fuels are contributing to a recently observed engine nozzle fouling occurrence in field-deployed aircraft. The jet fuel samples were to be analyzed for inter-sample compositional differences as well as to determine if these fuels contain chemical constituents not normally found in military jet fuels that could be contributing to the observed engine nozzle fouling problem.

2.0 BACKGROUND

In our ongoing chemometric fuel property modeling program at the Naval Research Laboratory¹, we have been developing methodologies to predict fuel properties from compositional analyses from near-infrared (NIR) spectroscopy, Raman spectroscopy, capillary gas chromatography (GC) and combined gas chromatography-mass spectrometry (GC-MS). As part of this work, we have been developing a fuel property database, which currently is comprised of 240 worldwide jet fuels. In this effort, these chemometric techniques were employed to examine a group of fuel samples taken from the fuel supply system at Aqaba and the USMC air station at Al Asad, Iraq.

This examination was conducted at NRL as part of an ongoing investigation by NAVAIR to determine if fuel contaminants are contributing to premature fuel nozzle coking on USMC KC-130J and USAF C-130J aircraft deployed in Iraq. Analysis of fouled fuel nozzles performed by the engine manufacturer had revealed the presence of traces of polymeric organic compounds tentatively identified as a polymer and plastisizer. There are many potential sources of such polymeric fuel contaminants in the fuel handling and distribution system, including fliters, gaskets, and other polymer-based components. Another potential source identified was a polymer-based dust abatement solution that was deployed on the airfield where the nozzle fouling was occurring to minimize sand and dust transport into the engines.

3.0 EXPERIMENTAL

The 26 jet fuel samples presented for examination were subjected to several analytical methods: gas chromatography with flame ionization detection (GC-FID), gas chromatography with mass-selective detection (GC-MS), and near-infrared (NIR) spectroscopy. Compositional data from the 26 fuel samples were analyzed by principle component analysis (PCA) to determine if there were any detectable compositional differences between the fuels within the sample set, and between this set and specification jet fuels normally encountered. Thermal oxidation rates of three of the USMC fuel samples were measured and compared to autoxidation of typical jet fuels.

¹ Morris, R. E.; Johnson, K. J.; Hammond, M. H.; Rose-Pehrsson, S. L. "The Development of Advanced Sensor Technologies to Measure Critical Navy Mobility Fuel Properties". NRL Memorandum Report NRL/MR/6180—06-8937. Naval Research Laboratory, January 27, 2006.

The fuel samples were also examined for the presence of a provided sample of Envirotac II®, a commonly used dust abatement polymer.

Test Fuels. A group of 26 U.S. Marine Corps JP-8 jet fuels, shown in Table I, were submitted to NRL for compositional analysis. These fuels were acquired from the DESC storage facility at Aqaba, Iraq on 25 December 2005 and from the USMC base at Al Asad, Iraq on 30 December 2005, at various locations throughout the fuel supply chain. Samples were provided to NRL in 40 mL quantities for this examination. In addition to these 40 mL aliquots, 1-liter quantities of samples 10, 12, 16, 18 and 23 were provided for oxidation rate measurements as well as a 40 mL sample of a recently acquired JP-8 sample from the fuel supply at the Patuxent River Naval Air Station in Patuxent River, Maryland, which was provided for comparison.

Table 1. Set of 26 fuels sampled from the Al Asad fuel supply chain.

Sample#	Location	Sampling Point		Date Sampled
21	DESC Storage Aqaba	Tank Sample	Tank # 41	12/25/2005
22	DESC Storage Aqaba	Loading Arm Sample	Tank #38	12/25/2005
23	DESC Storage Aqaba	Tank Sample	Tank #39	12/25/2005
24	DESC Storage Aqaba	Loading Arm Sample	Tank #39	12/25/2005
25	DESC Storage Aqaba	Tank Sample	Tank#38	12/25/2005
26	DESC Storage Aqaba	Loading Arm Sample	Tank # 41	12/25/2005
12	Delivering To Al Asad	Truck	#12035 Trailer # 15346	12/30/2005
19	Delivering To Al Asad	Truck	#133484 Trailer # 12148	12/30/2005
17	Al Asad - KBR Bulk Fuel Farm	Storage #2 Bag #3	MPC Bag	12/30/2005
20	Al Asad - KBR Bulk Fuel Farm	Distribution Bag #1	GTA Bag	12/30/2005
10	Al Asad - CLB 2	Tank Farm #4	MPC Bag	12/30/2005
11	Al Asad - CLB 2	Tank Farm #5	Bell Avon/Reliance Bag	12/30/2005
4	Al Asad - MWSS 272	Storage/Truck Fill Bags	#1	12/30/2005
5	Al Asad - MWSS 272	Storage/Truck Fill Bags	#4	12/30/2005
8	Al Asad - MWSS 272	Storage/Truck Fill Bags	#2	12/30/2005
15	Al Asad - MWSS 272	Storage/Truck Fill Bags	#3	12/30/2005
3	Al Asad - MWSS 272	KC-130 Issue Bags	Juliet Bag #1	12/30/2005
18	Al Asad - MWSS 272	KC-130 Issue Bags	Juliet Bag #2	12/30/2005
1	Al Asad - MWSS 272	Refueling Truck	M970/ 502755	12/30/2005
2	Al Asad - MWSS 272	Refueling Truck	ARC/ 607305	12/30/2005
6	Al Asad - MWSS 272	Refueling Truck	M970/ 548349	12/30/2005
7	Al Asad - MWSS 272	Refueling Truck	ARC/ 607319	12/30/2005
13	Al Asad - MWSS 272	Refueling Truck	ARC/ 607308	12/30/2005
14	Al Asad - MWSS 272	Refueling Truck	ARC/ 607357	12/30/2005
9	Al Asad - VGMR 252	KC-130 Aircraft	VGMR 252 738/165738 Rt Wing Tk #4	12/30/2005
16	Al Asad - VGMR 252	KC-130 Aircraft	VGMR 252 381/166381 left Wing Tk #2	12/30/2005

NIR Spectroscopy. Near-infrared (NIR) spectra were obtained with a Cary model 5E spectrophotometer. Supracell cells with a path length of 10 mm were used. Spectra were obtained over the wavelength range from 1000 to 2300 nm, with a resolution of 1 nm. Data were collected with the Cary software provided with the instrument, and exported in comma separated value (CSV) format. The resultant numerical representations of the spectra were imported into MATLAB and combined in one array for subsequent Chemometric analysis.

Capillary GC Analysis. Gas chromatographic analysis was performed with an Agilent 6890N gas chromatograph with flame ionization detection. An autosampler injected 1.0 µL aliquots of each neat fuel sample into a split-splitless injector at 250°C with a split ratio of 60:1.

Chromatographic separation was provided by a 50 m x 0.2 mm Agilent HP-1 (100% polydimethylsiloxane) capillary column. During a sample run, the GC oven temperature was held at 50°C for one minute, then raised to 290°C at 10°C/min, holding for seven minutes at 290°C. This temperature profile led to a run time of 32 minutes. Flame ionization currents were acquired at a rate of 50 hz during the run. Following acquisition, the GC-FID chromatograms were extracted from the Agilent datafiles and imported into MATLAB using an in-house program. Data were assembled in to a single double precision array for Chemometric analysis.

GC-MS Analysis. The fuel samples prepared by diluting 2 µL of each sample with 2 mL dichloromethane. An autosampler injected 1.0 µL aliquots of each of five replicate samples in random order to an Agilent model capillary gas chromatograph with a mass selective detector. A split/splitless injector at 250°C with a split flow ratio of 60:1 was used along with a 30 m x 0.25 mm Agilent HP-5 (dimethylpolysiloxane with 5% phenyl substitution) capillary column. The oven temperature profile began at 35°C and ramped up to 175°C at 4°C/min following this, the oven temperature was ramped up to 305°C at 70°C/min, and was held at 300 °C for seven minutes, giving a run time of approximately 42 minutes. A solvent delay of three minutes was used which reduced the data acquisition time to 39 minutes per run. Masses were scanned from m/z of 40 to 400. The GC-MS data that were acquired from these runs was converted from the native Agilent Chemstation data files to raw text format utilizing an in-house written MS Windows program. The chromatograms were then aligned to one another to minimize retention time variations from sample to sample and imported into MATLAB for chemometric analyses. The fuel dataset was examined for compositional differences by the ANOVA and factor analysis procedures.

Chemometric Analysis. Chemometric analyses of GC and NIR data were performed in MATLAB version 7.0 (The Mathworks, Inc., Natick, MA). Hierarchical cluster analysis was used to probe for evidence of sample clustering in the native measurement space of the GC and NIR data acquired. Principal components analysis (PCA), a factor analysis tool, was employed to determine if there were significant compositional differences detected within the 26 fuels by GC and NIR, and if so, to examine what data features are correlated with this compositional difference. By constructing a PCA model for these fuels, compositional similarities among samples are depicted by the clustering in a plot of the PCA “scores” which are the geometric projections of each sample’s chromatogram (or spectrum) onto each principal component axis of the model. Thus, the closer the PCA scores for different fuel samples, the more similar they are. In addition, a Hotelling T^2 statistic was computed that describes the fit of samples within the model. Samples that fall outside of the confidence interval for this model can be considered significantly different. In this way, the compositional similarities of each of the 26 fuel samples were determined. In addition to being compared against each other, compositional data of the 26 USMC fuel samples was also compared with the NRL-IPT fuels database developed as part of the ongoing fuel chemometric sensor development program. This fuel database, at the time of this analysis, contained data from roughly 200 specification JP-8 and Jet A fuels collected from around the world. By projecting data from the 26 USMC fuel samples onto a PCA model built with the fuels in the NRL-IPT database, the compositional similarities of these fuels with “typical” specification fuels was assessed. PCA analysis was conducted utilizing algorithms contained in the PLS Toolbox for MATLAB. (Eigenvector Research, Inc., Manson, WA) Prior to PCA analysis, imported GC or NIR data was mean-centered.

ICP-AES Elemental Analysis. An elemental survey was conducted on all 26 USMC fuel samples by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). These analyses were conducted by NAVAIR and the results were provided to NRL for comparison with the compositional analyses performed in-house.

Autoxidation Rate Measurements. Oxygen content in stressed fuel effluent samples was determined by gas chromatography as described elsewhere.^{2,3} Dissolved gases were separated on a 6 ft. x 1/8 in. stainless steel column packed with 60/80 mesh 5X molecular sieves (Supelco). This was followed by a second 6 ft. x 1/8 in. stainless steel column packed with 42/60 mesh alumina, to prevent interference from organics in the detector. Column temperatures were maintained at 100°C and entrapped organics were periodically backflushed from the alumina column at elevated temperatures. Oxygen, nitrogen and argon were detected in the effluent with a temperature regulated discharge helium ionization detector (Gow-Mac, model 24-600). Under these conditions, oxygen and argon eluted simultaneously, and the signals were corrected for argon content, from measurements taken after all the oxygen was consumed (typically at 300°C or greater). To maintain sufficient sensitivity for oxygen, the helium carrier gas for the HID was purified with a heated diffusion cell (Electron Technology, Inc.). Detector response was calibrated with air, and standards containing 0.5 and 5.0% oxygen in helium. Liquid sample volumes (10 µL) were corrected for changes in temperature and atmospheric pressure and introduced into the chromatograph with a liquid sampling valve. All results were calculated from a minimum of three measurements.

Detection of dust abatement polymer. A sample of the Envirotac II® soil stabilizer was obtained from the manufacturer (Environmental Products & Applications, Inc., Palm Desert, CA 92260) to facilitate the examination of the fuel dataset for the presence of this material. The Envirotac II® is supplied as an aqueous emulsion of an acrylic copolymer and is used to control dust and sand injection in aircraft. The acrylate polymer was isolated from the emulsion by partial evaporation of the liquid phase. This material was not found to be soluble in fuel and was only dissolved in the methylene chloride after warming and sonication. A sample of 5 mg of Envirotac II® was dissolved in 1 mL of methylene chloride and examined by GC-MS, which revealed the presence of a characteristic ion at $m/z=221$.

4.0 RESULTS AND DISCUSSION

The PCA scores from NIR analysis of the 26 USMC fuels and the JP-8 fuel sample from the Patuxent River NAS, in relation to the reference fuels database is shown in Figure 1. Note that all the test fuels are clearly within the clustering of the reference specification fuels, indicating that these fuels are compositionally similar to typical specification jet fuels. Also note that the JP-10 and a priming fluid are well outside of the 95% confidence limit for the PCA model, indicating that these are significantly different in composition. This is as expected, since these two samples are pure hydrocarbons, and thus, very different compositionally from normal JP-8 fuels.

² Hazlett, R.N.; Hall, J.M.; and Matson, M. *Ind. Eng. Chem., Prod. Res. Dev.*, 2(16), 171, **1977**.

³ Morris, R.E., Hazlett, R.N. *Ind. Eng. Chem. Res.* 27(8), 1524, **1988**

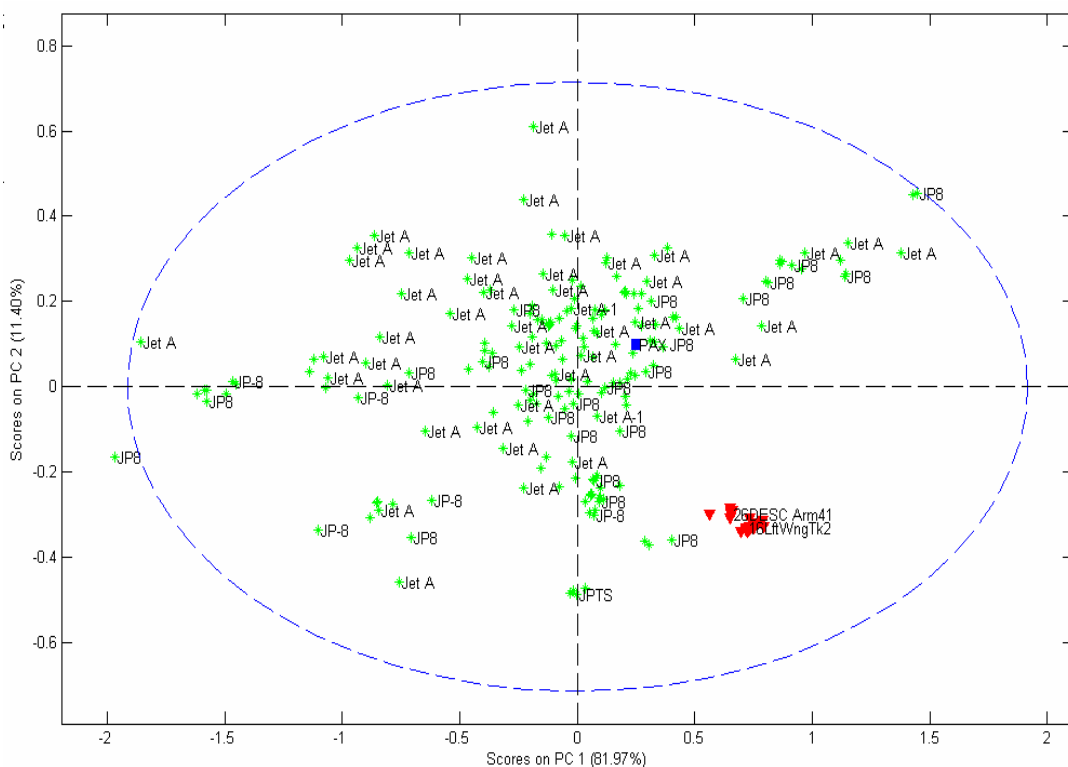


Figure 2. Scores plot from PCA of USMC fuels (in red), compared to reference fuels (green) and the PAX JP-8.

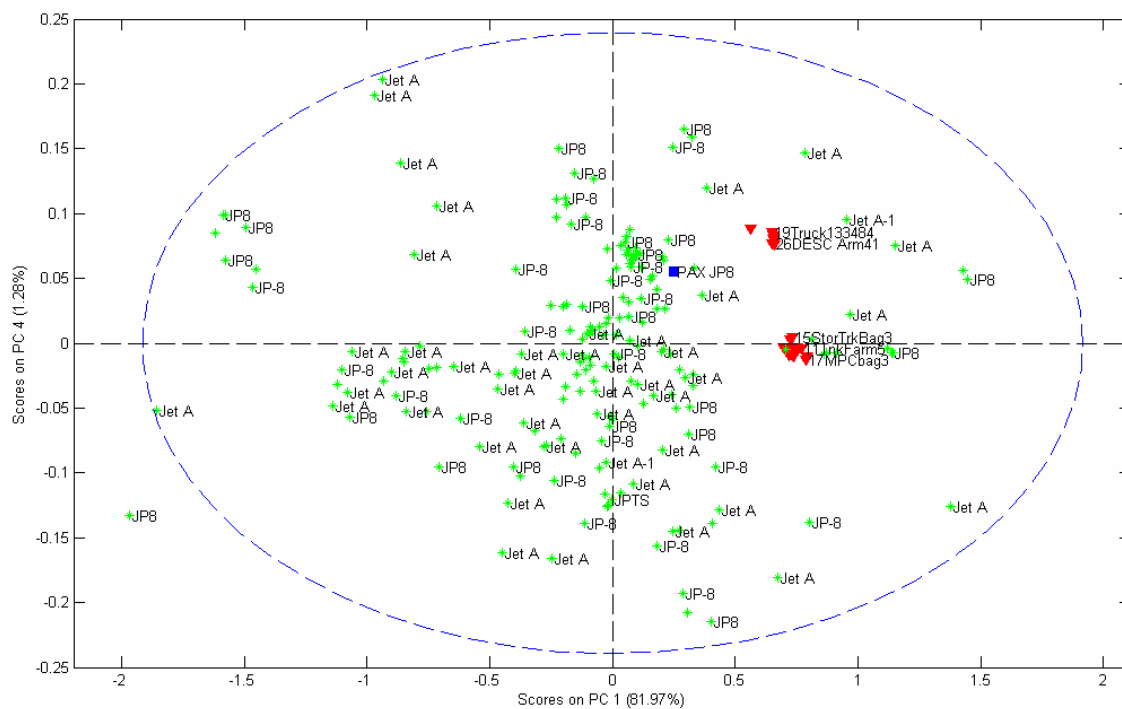


Figure 3. Scores plot of PC4 vs PC1 from PCA of the USMC fuels (in red), compared to reference fuels (green) and the PAX JP-8, showing similarities to reference fuels and discrimination of two batches within the USMC JP-8 fuel set.

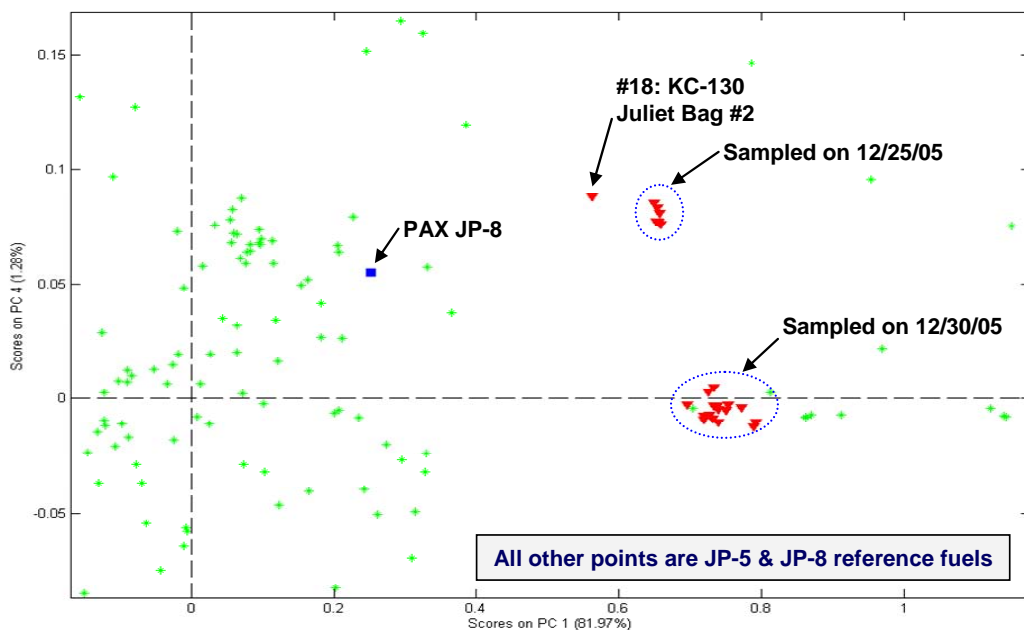


Figure 4. Detail from Figure 3, showing a clear distinction between the fuels sampled from the supply depot on December 25 and the fuels sampled at Al Asad on December 30, while still within the normal fuel composition range of the reference fuels.

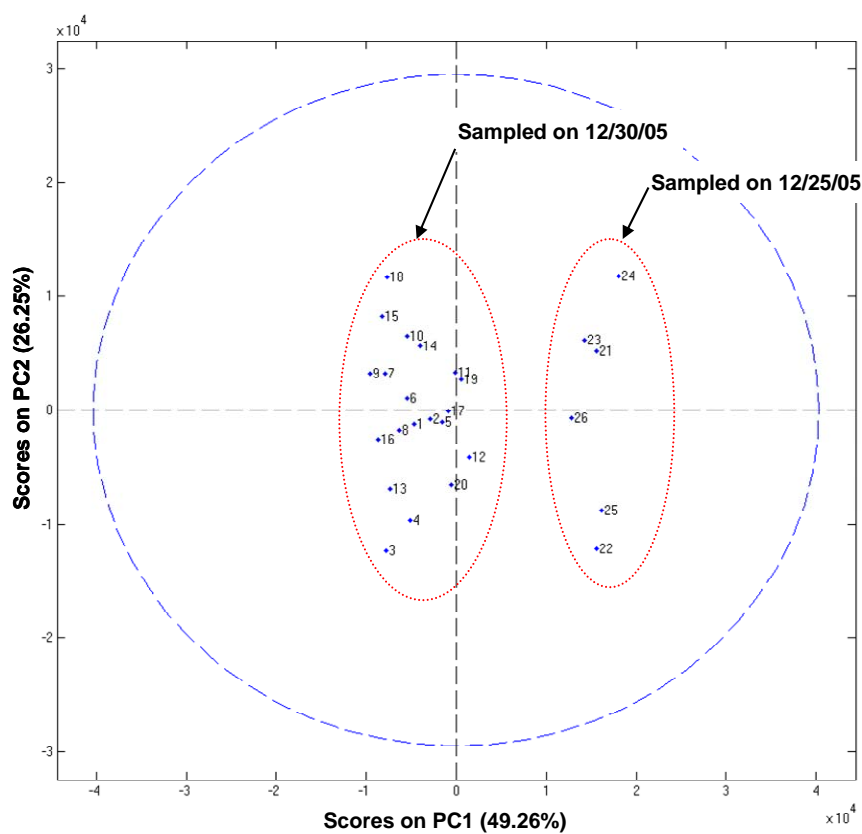


Figure 5. Scores plot from PCA of GC data, showing distinction between fuels sampled on two different dates, similar to that previously seen in scores plots of NIR data.

Table 2. ICP-AES elemental analyses of the fuel sample set, showing those elements detected used in the PCA. Elements analyzed for and found to be below the lower detection limits were not used for PCA. Results are given in µg/kg (Data provided by NAVAIR).

Sample #	#01	#02	#03	#04	#05	#06	#07	#08	#09	#10	#11	#12	#13
Ag (Silver)	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.014	0.012	0.008	0.008
Al (Aluminum)	<0.019	<0.019	<0.019	<0.019	<0.019	<0.019	<0.019	<0.019	<0.019	0.067	0.082	0.053	0.053
B (Boron)	0.093	0.072	0.045	0.075	0.047	0.075	0.038	0.076	0.031	0.145	0.134	0.079	0.087
Ca (Calcium)	0.019	0.012	0.016	0.017	0.013	0.011	0.016	0.014	0.015	0.022	0.014	0.016	0.014
Cd (Cadmium)	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.005	0.004	0.005	0.004
Cu (Copper)	0.005	0.004	0.009	0.004	0.003	0.003	0.004	0.004	0.006	0.005	0.004	0.006	0.003
K (Potassium)	<0.076	0.095	0.091	0.084	0.098	0.105	0.123	<0.076	<0.076	<0.072	<0.072	0.106	0.131
Li (Lithium)	<0.019	<0.019	<0.019	<0.019	<0.019	<0.019	<0.019	<0.019	<0.019	0.103	0.109	0.091	0.091
Mg (Magnesium)	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.001	0.003	0.002
Mn (Manganese)	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	<0.001	<0.001	<0.001	<0.001
Na (Sodium)	0.812	0.759	0.612	0.895	0.769	0.793	0.696	0.865	0.797	0.810	0.820	0.732	0.784
Ni (Nickel)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.012	0.012	<0.012	<0.012
P (Phosphorous)	0.116	0.085	<0.047	0.072	0.047	<0.047	<0.047	0.072	<0.047	0.195	0.182	0.154	0.130
Si (Silicon)	0.080	0.061	0.088	0.101	0.073	0.072	0.054	0.113	0.087	0.074	0.088	0.074	0.063
Ti (Titanium)	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.002	0.003	<0.002	0.002
V (Vanadium)	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.013	0.014	0.009	0.009
Zn (Zinc)	<0.003	<0.003	0.006	<0.003	0.005	<0.003	<0.003	0.003	0.006	0.010	<0.003	<0.003	<0.003

Sample #	#14	#15	#16	#17	#18	#19	#20	#21	#22	#23	#24	#25	#26
Ag (Silver)	0.009	0.007	0.007	0.008	0.007	0.011	0.008	0.011	0.011	0.009	0.008	0.009	0.007
Al (Aluminum)	0.064	0.052	0.055	0.052	0.049	0.069	0.056	0.065	0.052	0.045	0.044	0.054	0.043
B (Boron)	0.096	0.069	0.047	0.052	0.057	0.235	0.111	0.170	0.107	0.087	0.077	0.095	0.049
Ca (Calcium)	0.019	0.016	0.028	0.007	0.021	0.025	0.010	0.009	0.010	0.010	0.008	0.010	0.007
Cd (Cadmium)	0.004	0.004	0.014	0.004	0.004	0.006	0.008	<0.006	0.007	<0.006	<0.006	<0.006	<0.006
Cu (Copper)	0.003	0.003	0.003	0.002	0.003	0.004	0.004	0.002	0.003	0.001	0.003	0.003	0.002
K (Potassium)	0.081	<0.072	0.072	0.096	0.122	0.081	0.116	0.073	0.132	0.093	0.083	0.086	0.138
Li (Lithium)	0.101	0.096	0.078	0.090	0.086	0.066	0.063	0.060	0.061	0.054	0.051	0.056	0.037
Mg (Magnesium)	0.002	0.002	0.006	0.001	0.002	0.008	0.002	0.002	0.002	0.002	0.002	0.002	0.001
Mn (Manganese)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Na (Sodium)	0.833	0.801	0.700	0.737	0.734	0.640	0.619	0.586	0.591	0.520	0.532	0.501	0.375
Ni (Nickel)	<0.012	<0.012	<0.012	<0.012	<0.012	<0.018	<0.018	<0.018	<0.018	<0.018	<0.018	<0.018	<0.018
P (Phosphorous)	0.161	0.123	0.127	0.131	0.136	0.256	0.217	0.209	0.195	0.170	0.163	0.142	0.135
Si (Silicon)	0.070	0.066	0.078	0.068	0.065	0.084	0.077	0.090	0.070	0.072	0.063	0.066	0.063
Ti (Titanium)	0.002	<0.002	0.002	<0.002	0.002	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
V (Vanadium)	0.010	0.009	0.007	0.007	0.008	0.009	0.005	0.006	0.006	0.003	0.003	0.003	<0.003
Zn (Zinc)	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.016	<0.003	0.003	<0.003	0.010

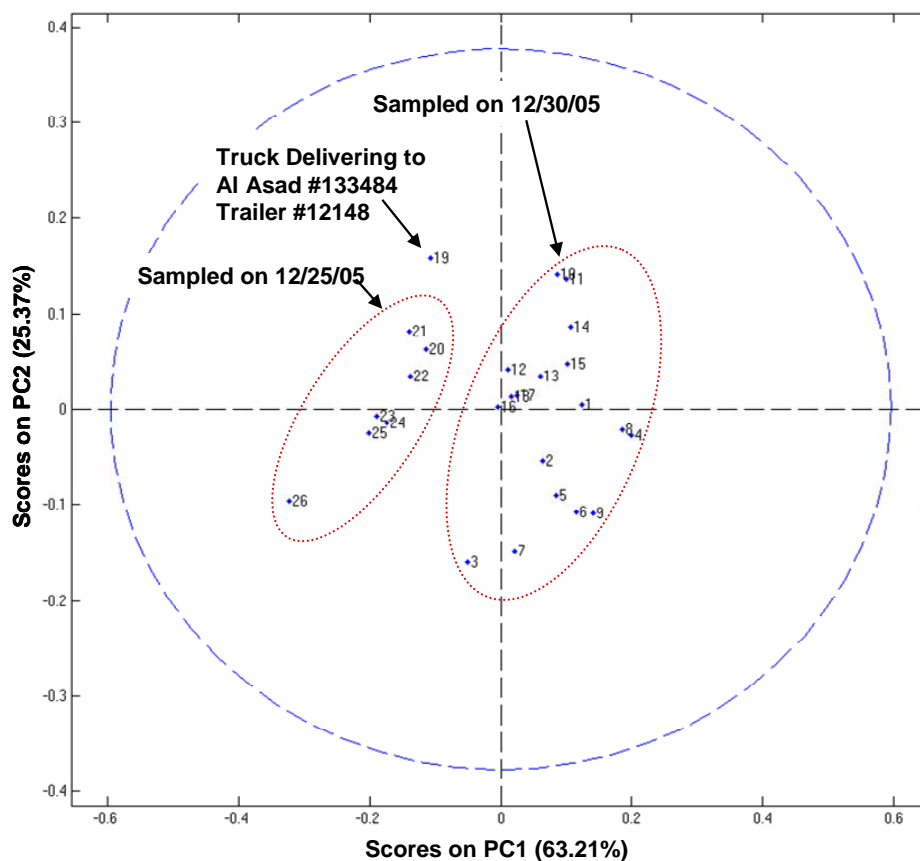


Figure 6. Scores plot from PCA of ICP-AES data, showing similar distinctions between the two different fuel batches.

This illustrates that this approach is sufficiently sensitive to discriminate between different fuel deliveries, and thus it would be expected to easily discern the presence of contaminants. Since all the fuels were shown to be similar in composition to the reference fuels by both GC and NIR spectroscopy, these findings indicate that there are no contaminants in any of the USMC fuel samples.

In Figure 7, the oxygen consumption of samples #23, #16 and #8 are shown, in comparison with several JP-5 fuels examined in a previous study. The data are shown as the percent of initial dissolved oxygen vs the fuel temperature as the fuel leaves the JFTOT heater tube holder. As shown, the USMC fuels fell within the normal range of oxidation temperatures and rates observed for specification JP-5 fuels. There is some indication that fuel #23 is slightly more thermally stable than the other two USMC samples, as shown by the higher oxidation onset temperature, but this is still within the normal range. For comparison, similar data from a copper contaminated fleet fuel sample and an aged fuel from storage are shown. These fuels are less thermally stable, and this is clearly shown by the lower oxidation onset temperatures. These findings indicate that the USMC fuels examined are not more prone to thermal oxidation than a typical specification jet fuel.

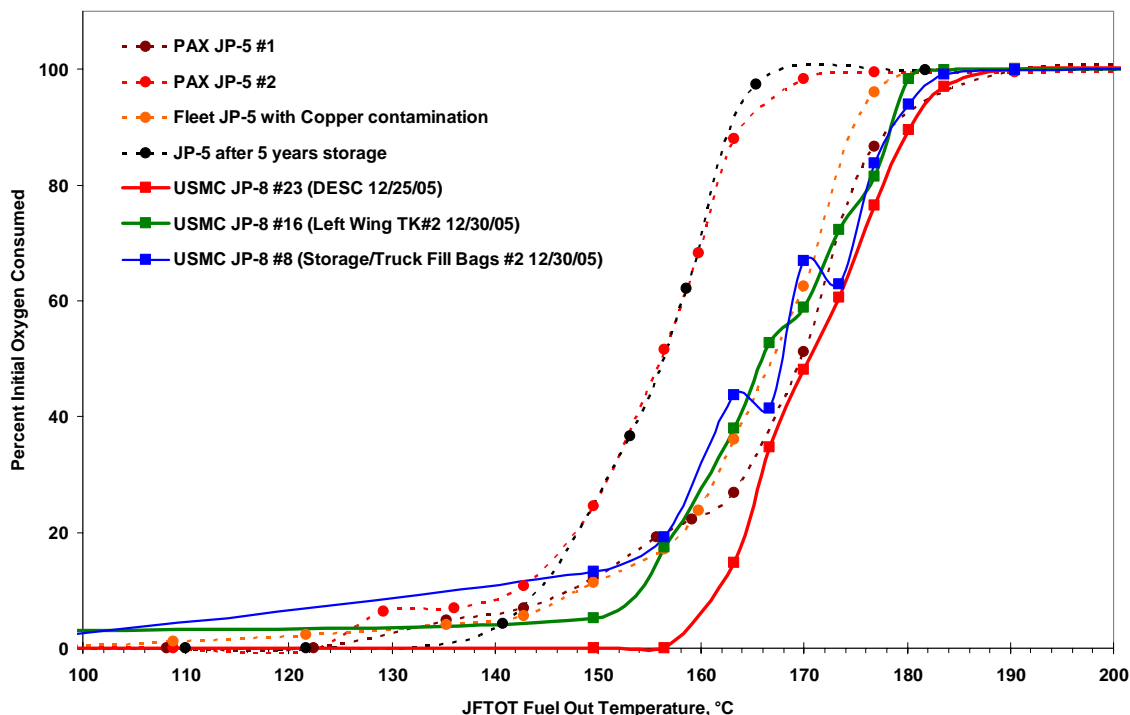


Figure 7. Oxygen consumption of the USMC JP-8 fuels, showing similar thermal autooxidation stability characteristics compared to specification JP-5 fuels. A thermally unstable fleet sample contaminated with copper and an aged fuel sample are also shown for comparison.

GC-MS analysis of the 26 USMC JP-8 fuels did not indicate any detectable compositional differences within the precision of the instrument that were inconsistent with typical batch-to-batch fuel variations. There were no indications of abnormal fuel components or contaminants. The presence of the Envirotac II® in the USMC JP-8 fuels was examined by monitoring for the characteristic $m/z=221$ ion from fragmentation of the polymer in the GC-MS analysis. Figure 8A shows the total ion chromatogram (TIC) of the Envirotac II® in methylene chloride in comparison with neat methylene chloride. Comparison of the TIC of the Envirotac II® in methylene chloride in Figure 8B with the corresponding TIC of fuel #5, shows that the polymer was not detected in this fuel. Similar analysis of the remaining 25 USMC fuels showed no evidence of the Envirotac II® or any other detectable contaminants.

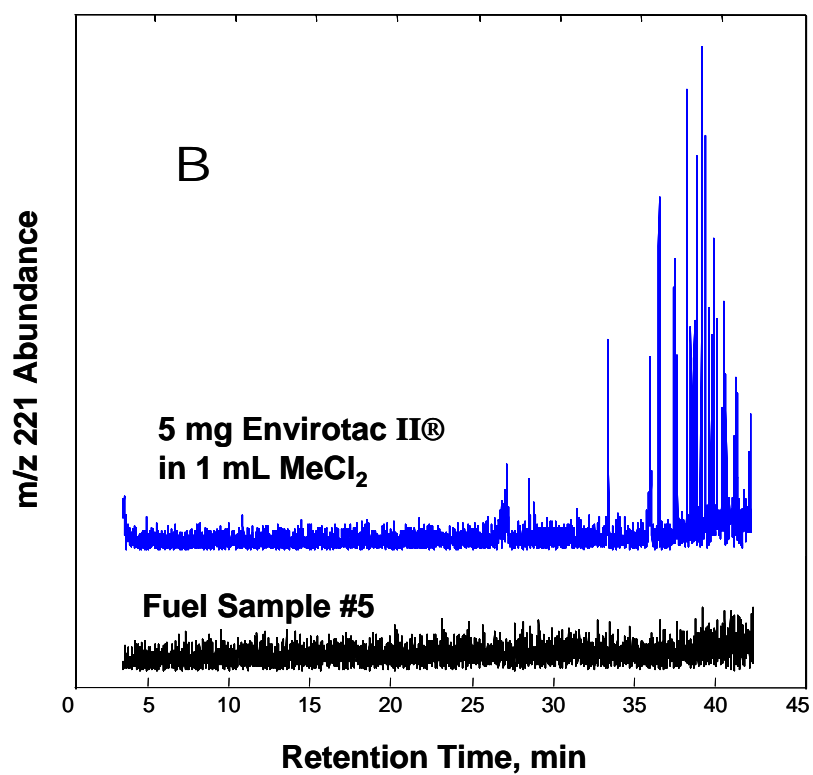
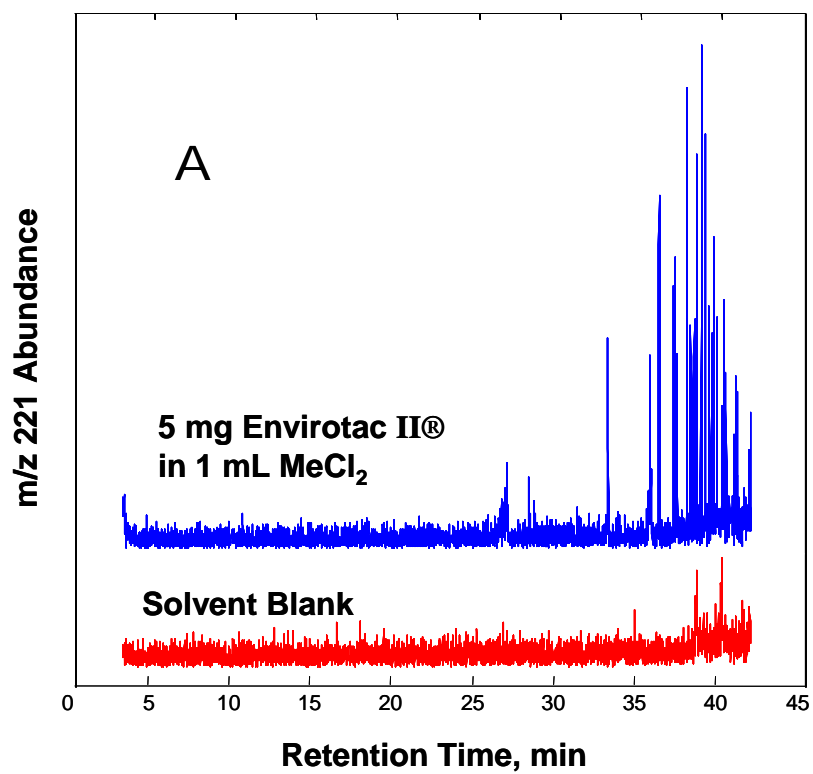


Figure 8. Detection of Envirotac II® by GC-MS through selected ion monitoring of the characteristic fragment at $m/Z=221$, compared to neat methylene chloride (Fig. 8A) and to fuel sample #5 (Fig. 8B).

5.0 SUMMARY

The findings of this study can be summarized as follows:

- PCA analysis of GC-FID and GCMS chromatograms of the 26 fuel samples yielded results similar to those obtained with the NIR spectra, showing minor differences between fuels sampled on the two different dates.
- GC-FID analyses indicated only slight variations in the amounts of lighter fuel components between samples, consistent with batch to batch differences in fuels.
- ICP-atomic absorption analyses of the fuels revealed slight differences in overall elemental content of the two sample batches.
- GC-MS analyses indicated no apparent contamination of the examined fuel samples with a non-fuel adulterant, such as the Envirotac II® dust-abatement polymer.
- Oxygen consumption measurements did not show any significant differences in oxidation rates, which are indicative of thermal stability and are consistent with JFTOT results.

6.0 CONCLUSIONS

The overall chemical compositions of the 26 JP-8 samples were found by chemometric modeling to be within the range of compositions determined in the 240 worldwide JP-8, JP-5 and Jet A fuels in our reference fuels database. This result was obtained by both gas chromatography and NIR spectroscopy. However, there were some detectable differences in composition between the fuels sampled from the storage facility at Aqaba and those sampled further down the supply chain at the Al Asad airbase. This sampling discrimination was a consequence of slight differences in the proportions of lighter (i.e. lower molecular weight) fuel components present in all the fuel samples. These differences are consistent with normal batch to batch variations typically observed in jet fuel. This result illustrated the sensitivity of the PCA modeling technique to detect small differences in composition. While the two batches of fuels were slightly different, they were still similar to normal specification jet fuels. This batch discrimination was observed from the GC and NIR data, in addition to the elemental data from ICP analysis.

Analyses by GC, NIR and GC-MS did not detect the presence of detectable levels of any contaminants or otherwise abnormal fuel components. In particular, GC-MS was shown to be capable of detecting the presence of Envirotac II® dust abatement polymer, and was used to monitor for the presence of this polymer in the USMC-provided jet fuel samples. The results of this analysis indicated that this product was not present in any of the 26 provided USMC fuel samples.

7.0 ACKNOWLEDGEMENT

This work was funded by NAVAIR (AIR-4.4.5), through the Navy Fuels & Lubes Integrated Product Team (IPT). Elemental analyses were provided by Dr. Alice Huang of NAVAIR (AIR 4.4.6.1).